Synthesis and Characterization of $BaMnO_3$ Multiferroic Ceramics

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Certificate

This is to certify that the work in the thesis entitled "**Synthesis and Characterization of $BaMnO_3$ Multiferroic Ceramics**" submitted by **Miss Rashmi Rekha Sahoo** is a record of an original research work carried out by her under my supervision and guidance in partial fulfilment of the requirements for the award of the degree of Master of Science in Physics. This thesis has not been submitted for any degree or academic award elsewhere.

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DECLARATION

I hereby declare that the work carried out in this thesis is entirely original. It was carried out by me at Department of Physics and Astronomy, National Institute of Technology, Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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ABSTRACT

In the present study, $BaMnO_3$ ceramic oxide has been prepared and analysed using various experimental techniques. The proposed material has been prepared using high temperature solid state reaction route. The structural (XRD), microstructural (FESEM), compositional (EDX) and dielectric properties have been studied extensively. X-ray diffraction (XRD) analysis confirms the formation of compound. Field Emission Scanning Electron Micrograph (FESEM) shows thenon-homogenous distribution of grains ranging from 1-1.5μmwhich are densely packed. Energy Dispersive X-ray (EDX) spectroscopic analysis shows the presence of all the elemental in $BaMnO_3$. The ferroelectric to paraelectric phase transition is observed from temperature dependent dielectric analysis. The loss tangent is found to be increases with increase in temperature. DC and AC conductivity decreases with increase in temperature.

INTRODUCTION: CHAPTER 1

Magnetoelectric multiferroic materials are technologically and fundamentally important due to the exciting fundamental physics and various device applications such as sensors, multilayer capacitors, as well as in multiple state memory devices. According to the definition of H. Schmit, crystals are said to be multiferroic when more than one primary ferroic order parameter are present in same phase. The primary ferroic order parameters are ferroelectric, ferromagnetic and ferroelestacitiy. The research and development of multiferroic materials are deals with the identification of many unusual or rare mechanism [1].

1.1. Primary Ferroics:

Ferromagnetism: Ferromagnetic material undergoes a phase transition from a high temperature phase which doesn't have a macroscopic magnetic moment (i.e., paramagnetic) to a low temperature phase which has a spontaneous magnetisation even in the absence of applied magnetic field [2].

Ferro electricity: In case of Ferroelectric materials, the phase transition occurs from a high temperature state (paraelectric) to a low temperature phase (ferroelectric) which has a spontaneous polarisation whose direction can be switched by the application of electric field. They possess hysteresis response to an applied electric field. The most extensively studied ferroelectrics oxides belong to perovskite structure. Below Curie temperature, the spontaneous polarisation observed in ferroelectrics are derived from electric dipole moment due to the off-centring of B-site cations.[2]. Ferroelectric materials have two stable minima where the macroscopic polarisation is in opposite direction which can be enhanced via the application of external field. These two states can be denoted as 0 & 1 same as Boolean algebra. A single bit of memory can be based on a 0 or a 1 hence ferroelectric materials can be used in memory devices[3].

Ferroelasticity: Ferroelastic materials are those which exhibit a spontaneous strain even if the absence of stress [4].

1.2. Multiferroics:

Materials in which two or more ferroic order parameter occurs in the same phase. If the spontaneous magnetisation can be changed by an applied electric field and the spontaneous

polarisation can be reoriented by an applied magnetic field then the materials are called magnetoelectric [2].

1.3. Requirement for MagnetoelectricMultiferroicity:

Materials are said to be multiferroelectrics when they showed both ferromagnetic andferroelectric ordering in a single phase [2]. Due to the chemical incompatibility and mutual excusive nature of both the ordering, multiferroics are rare in nature. The existence of limited multiferroics are due to the following consideration:

Symmetry: Primary requirement for a material to be ferroelectric (due to the existence of sponanteous polarization) should belong to a non cetrosymmetric point group. Out of 32 point groups only in thirteen point groups allowing the existance of multiferroics properties [2].

Electrical Property: Ferroelectricmaterial mustbe an insulator but ferromagnets doesn't require specific electrical property and are often metals [2].

Chemistry of "d°-ness": In perovskite structure, the d orbital electronic configuration on the "B" sitecation play a crucial role for the materials to be ferroelectric or ferromagnetic.The partially filled d orbitals are responsible for magnetic ordering, where d^0 electronic configuration is responsible for ferroelectric ordering.

1.4. Symmetry and Multiferroicity:

Symmetry is closely related with multiferroicity.The ferroic properties can be characterised by their behaviour under space and time inversion.Space inversion will reverse the direction of polarisation "P" leaving the sign of "M"i.e. the magnetisation.While in the time invariance sign of "P" remains invariant but the sign of "M" is reversed. Hence multiferroicsubstances require both time and space invariance.

PEROVSKITE STRUCTURE: **CHAPTER 2**

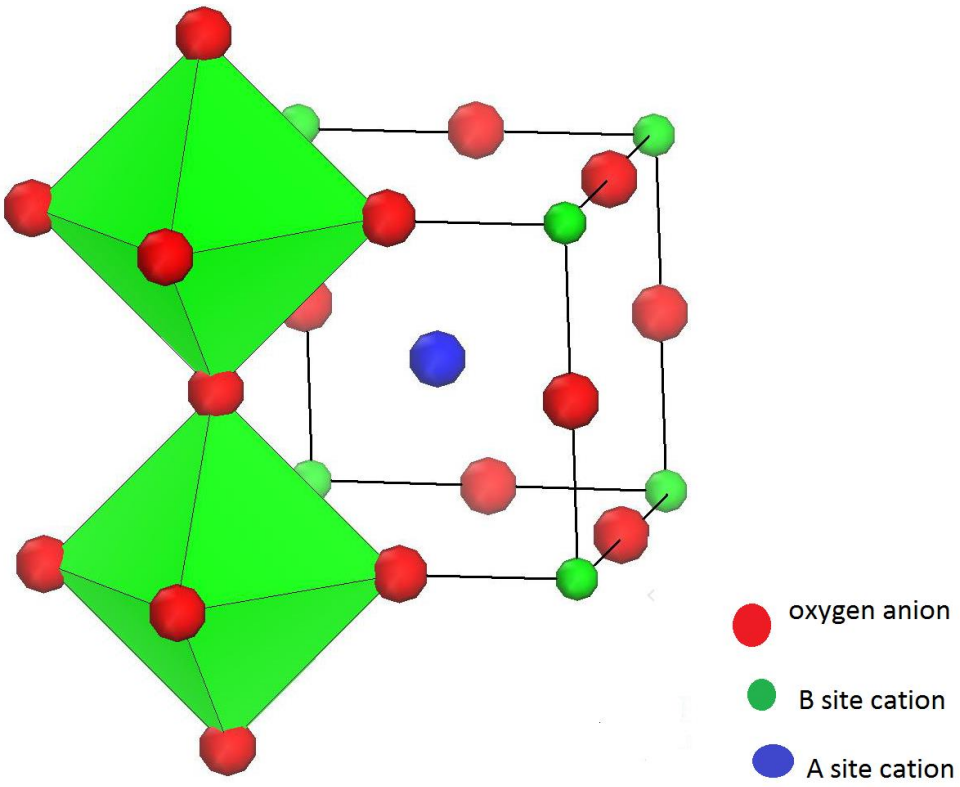


Fig.1. Structure of a typical perovskite structure

Perovskite structure have the general formula as ABO_3 where A and B are cations of different size and O is the anion.The A site cationis slightly larger than B cation.The B atom have 6 fold co-ordination number and the A atom have 12 fold co-ordination number as shown in Fig. 1.In general, A atom is placed at the corner i.e.(0,0,0), B atom is at the body centre i.e.(½,½,½) and theO atoms are at the face centre. The structure of an ideal perovskite shows that it isa network of corner shared BO_6 octahedral where all B-O- B angle are 180°. The structural distortion in perovskitecan be detected by the ratio of A and B ionic size and electronic configuration of the metal ions.

Generally two types of structural distortion are seen in perovskite i.e. off-centring of B

ion in the BO_6Octahedral and other is the tilting of BO_6 octahedral. The 1st type corresponds to displacive phase transition and the 2nd corresponds to order-disorder phase transition [4].

For an ideal cubic structure, the lattice parameter $a_\circ$ is [5]

$$a_\circ = \sqrt{2}(R_A + R_O) = 2(R_B + R_O)$$

Hence the Goldschmidt tolerance factor is

$$t = \frac{R_{A+R_O}}{\sqrt{2}(R_{B+R_O})}$$

When t<1 gives rise to tilting mode and when t>1 it shows off centring of smaller Bcation which causes tilting of BO_6 octahedron. The offcentring mainly occurs due to larger A and smaller B ion which leads to contraction of BO_6 octahedron. The BO_6 octahedra causes the formation of cavity where the B ion tilt better.

It has been found that perovskite oxides show high dielectric constant due to the collective polar displacement of the metal ion with respect to the oxygen octahedron. This property can be used as capacitive component in microelectronics[6].Another type ofperovskites have large dielectric constant are known as relaxor ferroelectrics. They also show frequency dispersion and a frequency dependent temperature maxima in temperature dependent dielectric properties.Now a days giant dielectric constant materials have great practical importance in electronic devices such as high energy density capacitor, MOSFET which eventually miniaturises the electronic devices.

The 1st discovered multiferroic material is Nickel iodine Boracite($Ni_3B_7O_{13}$I). Since then a large number of mutiferroics in different configuration have been studied. It is reported that $BaMnO_3$ shows both ferroelectric and ferromagnetic behaviour in the same phase, so it is called as multiferroic materials. Therefore $BaMnO_3$ is expected to be the potential candidate for multiferroicmaterilas.

LITRATURE SURVEY: CHAPTER 3

$BaMnO_3$ crystallize in to hexagonal perovskite structure due to its high tolerance factor. It is also reported that, $BaMnO_3$doesnot crystallise in the perovskite structure with corner-sharing oxygen octahedral. Due to the high Goldschmidt tolerance factor, $BaMnO_3$ stabilises in a hexagonal 2H structure without face sharing oxygen octahedra .With the increase in pressure, there will be decrease in the hexagonal behaviour, which leads to 4H structure. The 4H structure is an intermediate between 2H and cubic perovskietestructure [7].The assignment of the 2H phase of $BaMnO_3$at room temperature is carried out by Hardy and belongs to in polar $P6_3C_m$ space group[8]. However, Christensen and Ollivier reported that 2H $BaMnO_3$ belongs to $P6_3$/mmc space group[9]. B. L. Chanberlandet. al. reported the preparation condition and crystal structure of $BaMnO_3$ and $SrMnO_3$.They also reported the four probe electrical measurement on single crystal of $BaMnO_3$ from 4.2-298K and observed the semiconducting behaviour (ρ_{25K} =5.6× 10^5Ωcm $\&E_\alpha$ = 0.4eV). [10]. the preparation conditions such as temperature, pressure, reaction condition are also responsible for the crystal structure of $BaMnO_3$. [10-12]. S. Satapathyet. al. reported that the weak relaxor characteristic of $BaMnO_3$ (2H) form temperature dependent dielectric properties[13].C. G. Hu et. al. prepared single crystalline $BaMnO_3$ and $BaTi_{0.5}Mn_{0.5}O_3$nano rods using the composite-hydroxidemediated approach. They observed the phase transition from temperature dependent electrical resistivity [14].E. J. Cussen and P. D. Battle reported the crystal and magnetic structure of (2H) $BaMnO_3$[15]. J. Varignon and P. Ghosez reported the improper ferroelectricity and multiferroism in 2H $BaMnO_3$.It has also been seen that preparation of $BaMnO_3$ below 1150℃ leades to two layer structure, which is an antiferromagnetic. The long range AFM arises below Neel temperature . [1].

In view of the importance of the topic multiferroics, we have planned to prepare $BaMnO_3$. In the present case we have attempted to prepare single phase materials by optimizing the synthesis condition.

OBJECTIVES OF THE PROJECT: CHAPTER 4

The main aim of the project is to

(i) Synthesis of $BaMnO_3$ multiferroics using solid state reaction route.

(ii) To characterise the sample using the technique (a) to study the structural properties using XRD analysis, (ii) to visualize the surface morphology using FESEM, (iii) to study the elemental compositional analysis using EDX. And (iii) to study the dielectric properties with respect to frequency at different temperatures.

SYNTHESIS OF THE SAAMPLE: CHAPTER 5

5.1. Introduction:

There are various synthesis methods available in literature for preparation of the ceramic materials. Those methods are

(i) Mixed oxide process or solid state react1ion route

(ii) High energy ball milling process

(iii) Sol-gel method

(iv) Co-precipitation method

(v) Hydrothermal method

(vi) Combustion method etc.

All the above mention methods have their own advantage and disadvantages. Among all, mixed oxide process or solid state reaction route is widely acceptable due to its large scale production and low cost. In this study, $BaMnO_3$ have prepared using high temperature solid state route.

5.2. Mixed Oxide Method:

In mixed oxide method precursor powder (oxide or carbonate) are heated either in partial vacuum or under flowing oxygen. The preparation of the material consists of the following steps. The raw materials are first weighed according to the stoichiometric ratio. The raw materials are then thoroughly mixed (both dry and wet mixing) in an agate mortar in order to obtain a homogenous mixture. The mixture so obtained then put in a furnace to calcine in air. The calcination temperature is important as it influences the density and hence the physical properties of the final desired product. Usually, the temperature of calcination is chosen high enough to complete the reaction to form the material, but the high temperature calcination may affect volatile oxides. So, the calcination temperature should be optimized for both the completion of reaction as well as prevention of loss in volatile oxides in the final product. Double calcinations/re-calcinations step is useful to get a homogeneous and single phase compound. The calcined powders then cold pressed into cylindrical pellets by a hydraulic press with polyvinyl alcohol (PVA) as the binder. The use of the binder solution is to reduce brittleness of the pellets. The cold pressed specimens will then be sintered at higher temperature to achieve high density. Sintering is accompanied by the elimination of inter-granular voids and by compactness of the whole system.

5.3. Experimental Steps:

1. For the preparation of $BaMnO_3$ the constituents $BaCO_3$,MnO_2 were weighted as per the calculated stoichiometric ratio and grinded together in agate mortar and pestle for one hour. Then acetone was added to the powder and again grinded till the mixture dried up completely.

2. The mixture was calcined for six hours at 800℃ in a covered crucible and the phase formation was checked by XRD at room temperature.

3. Sample was again grinded then calcined for 900℃ and the phase formation was checked. Again the sample was grinded and calcined at 1000℃ and the phase formation was checked.

4. The calcined powders was mixed properly with polyvinyl alcohol, which acts as a binder. It gives some mechanical strength to the pellets formed out of it. It also reduces the brittle nature of the pellets. About 1-2 mm thick cylindrical pellets were prepared from the above powders by uniaxial pressing using a hydraulic press at 6×10^7 kg/m^2 pressure.

5. sintering of the pellets were carried out at atmospheric pressure and temperature of 1050℃ for six hours in air. This leads to better void elimination of the samples. The binder is burnt out during high temperature sintering.

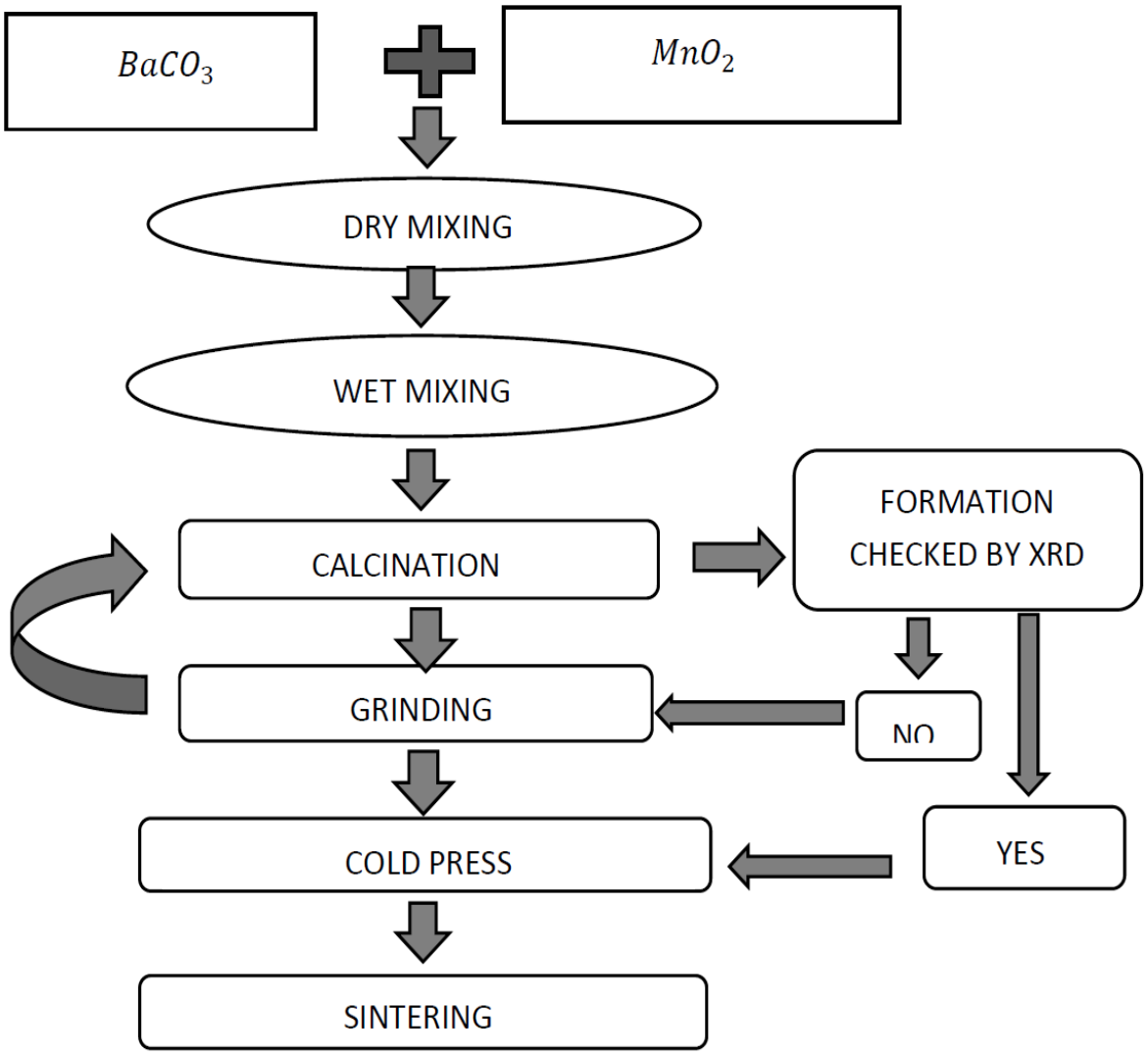


Fig. 2 Ray Diagram for the Synthesis of Sample

CHARACTERISATION TECHNIQUE: CHAPTER 6

6.1. X-Ray Diffraction:

X-ray diffraction is an analytical and non-destructive method for identification and quantitative analysis of any material. Here XRD was carried out using Rigaku Ultima IV diffractometer with Cu K_α radiation. The scanning range was chosen from 5° to 80° with scanning rate 3° per minute and 0.002° step size.

6.2. Field Effect Scanning Electron Microscope (FESEM):

It is an analytical method used in material science in order to study the topology, morphology, and composition of the material with much higher resolution. It has many advantages like it produces clear less electrically distorted images with spatial resolution 3-6 times better than that of conventional SEM. In order to study the surface morphology of the present sample NOVA NANO 450 has been used with 1000 kV applied potential. Due to the non-conducting nature of the sample it has been coated with thin layer of gold.

6.3. Energy Dispersive X-ray Spectroscopy (EDX):

It is an analytical technique used for the elemental analysis of a sample. When high energetic electron beam incident on the sample it emits X-rays. By investigating the nature of X-ray generated from the sample we can analyse the elements of the sample and also the amount of content of each element present in the sample. In the present study NOVA NANO 450 has been used.

6.4. Dielectric Analysis:

HIOKI IM3570 impedance analyser was used to measure the dielectric constant (ε') of the samples. To study the temperature dependent dielectric properties measurements were done in a wide range of temperature (room temperature to 400℃). The capacitance of the silver coated pellets made of the material under investigation was measured with 500mV perturbation potential in the frequency range 100Hz to 1 MHz. Dielectric constant (ε') was related to the measured capacitance (C) and geometric capacitance (C_0) of the prepared capacitors as C/C_0. Like ε', tan δ is also obtained at different frequency.

7.1. XRD Analysis:

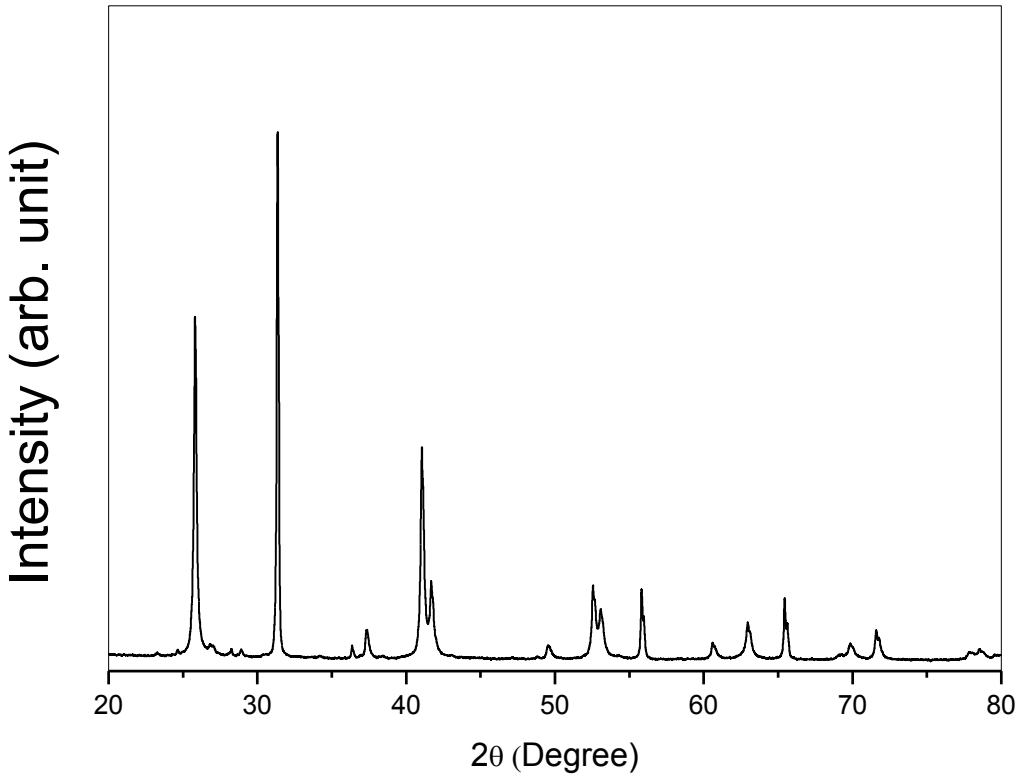


Fig. 3 X-ray diffraction pattern of $BaMnO_3$at room temperature

In order to check the formation of the compound we have carried out the XRD analysis. Fig. 2 shows the XRD pattern of calcined powder of $BaMnO_3$. The observed sharp and single defined peaks, which are different from precursors, suggesting the formation of the compounds with crystalline nature. The observed XRD pattern has been similar to that of the reported patterns suggesting the hexagonal crystal structure [13].

7.2. Field Effect Scanning Electron Microscopy:

F

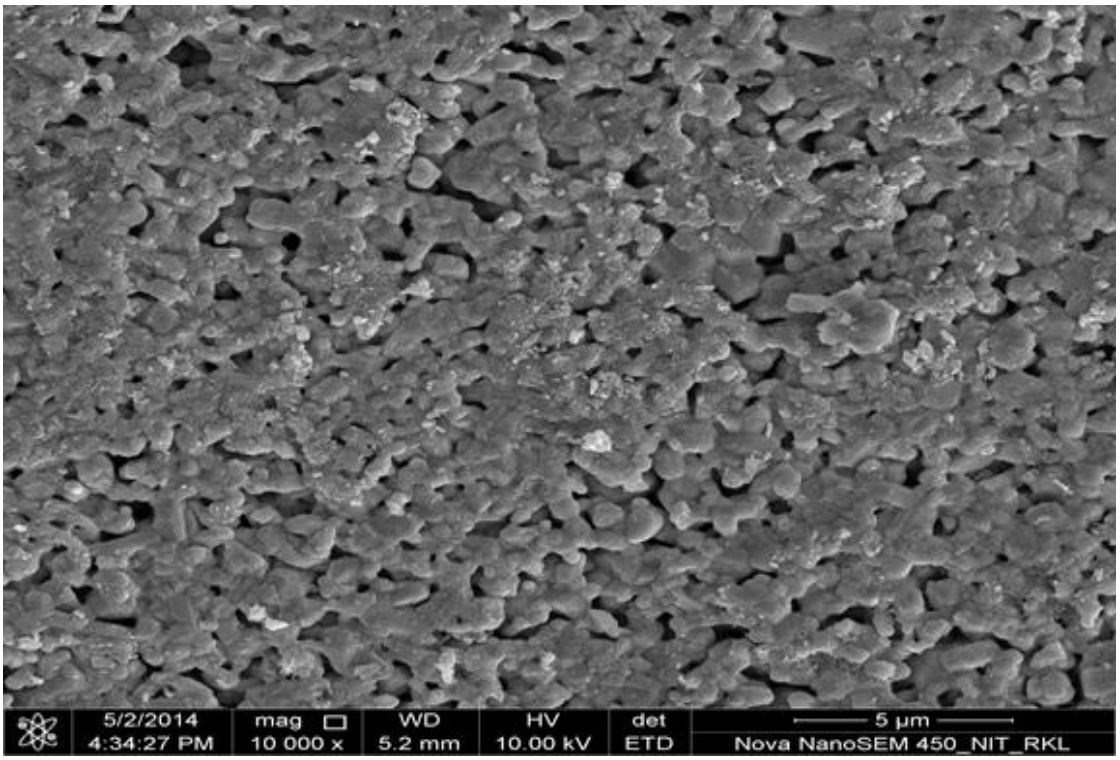


Fig.4. FESEM Micrograph of $BaMnO_3$

The surface morphology and topography of the material has been studied using FESEM analysis. Fig. 3 shows the FESEM micrograph of $BaMnO_3$. It has been observed that grains are of different size varying from 1-1.5 μm are non-uniformly distributed throughout the sample. There is very small number of voids which shows that the sample is well sintered and very dense.

7.3. Energy Dispersive X-ray Spectroscopy:

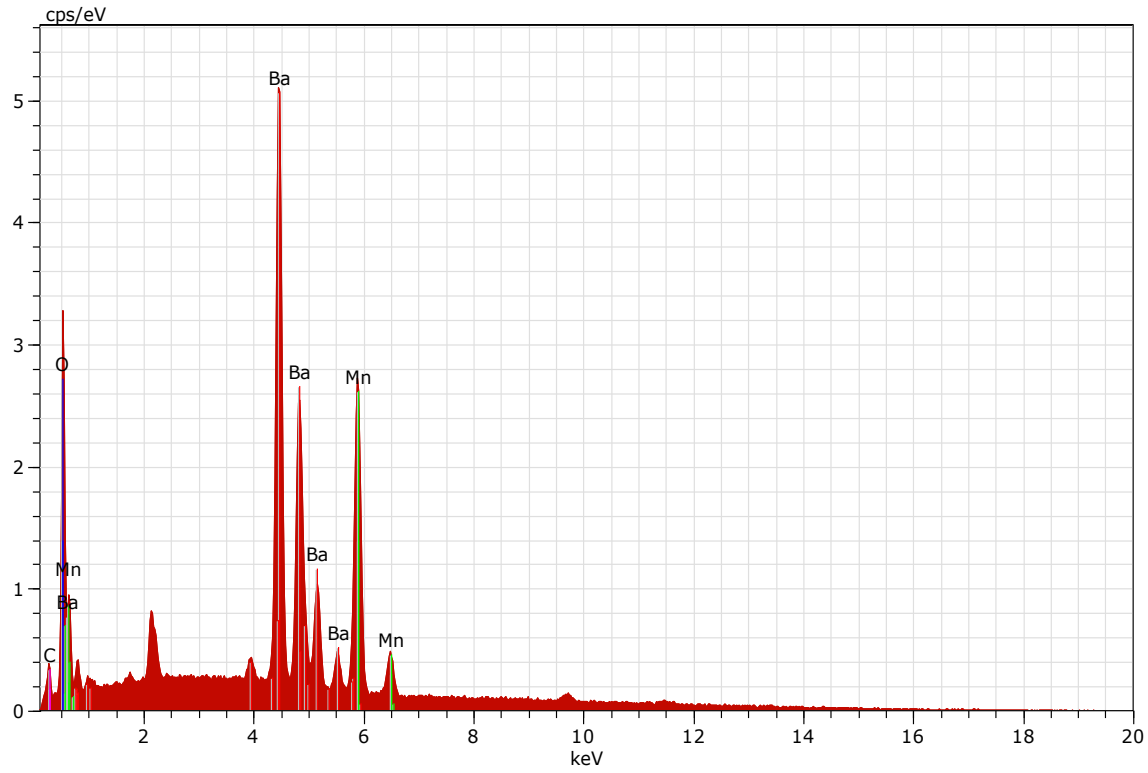
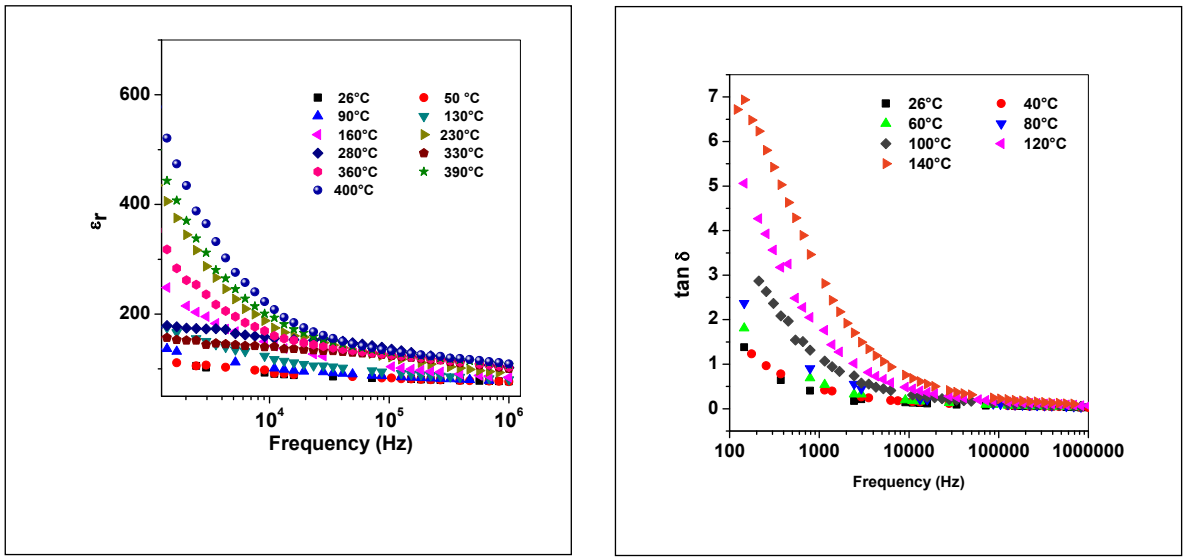


Fig. 5. EDX Analysis of $BaMnO_3$

In order to study the compositional analysis of the sample, we have carried out EDX analysis. And the pattern is shown in Fig. 5. The above figure confirms the presence of all the constituent elements in $BaMnO_3$.

7.4. Dielectric Analysis:

7.4.1 Frequency dependent Dielectric Study:

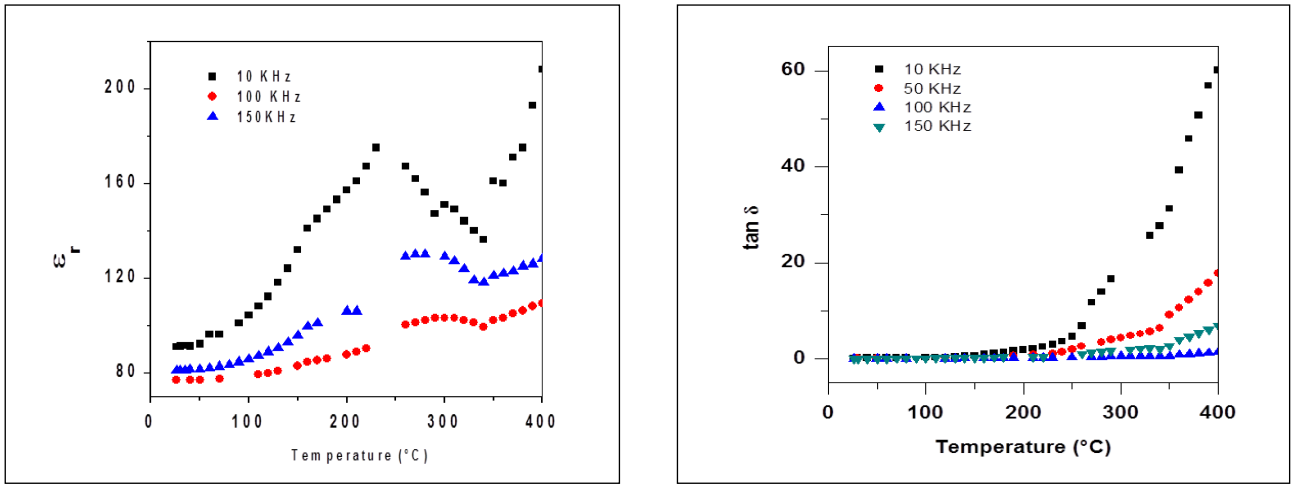


(a) (b)

Fig. 6. Frequency dependent (a) Dielectric Constant (b) Dielectric Loss

Figure 6 shows the variation of dielectric constant and loss tangent as a function of frequency at different temperature. It is observed that both the dielectric constant and loss tangent decreases with increase in frequency throughout the temperature range of investigations. As the frequency of field goes on increasing, different types of polarization fail one by one to make their full contribution thus resulting in dielectric dispersion. This dispersion leads to the decrease in the dielectric constant with rise in frequency. These types of behaviours are the typical behaviour of polar dielectrics.

7.4.2. Temperature Dependent Dielectric Properties:



(a) (b)

Fig.7. Temperature dependent (a) Dielectric constant (b) Loss Factor

Fig.7 (a) shows the temperature dependence of dielectric permittivity of $BaMnO_3$ at different frequencies (10 kHz, 100 kHz, and 150 KHz). It is observed that the dielectric constant increases with increase in temperature up to a certain value and with further increase in temperature it decreases. The temperature at which we observed the maximum dielectric constant is known as ferroelectric transition temperature. It is interesting to note that, the phase transition temperature for different frequency is different and shifted towards the higher temperature side with increase in frequency. This type behaviour of dielectric constant is the typical signature of relaxor behaviour. Similar type of behaviour has also been reported in literature [13].

Fig.7 (b) shows temperature dependent loss tangents at different frequencies. With increase in temperature the dielectric loss is nearly constant up to 250^0C and on and above that temperature dielectric loss increase sharply. At lower frequency range, the increase of loss factor is higher as compared to higher frequencies. The sharp increase in dielectric loss is due to conduction process [4].

7.4.3. Impedance Spectroscopic Analysis:

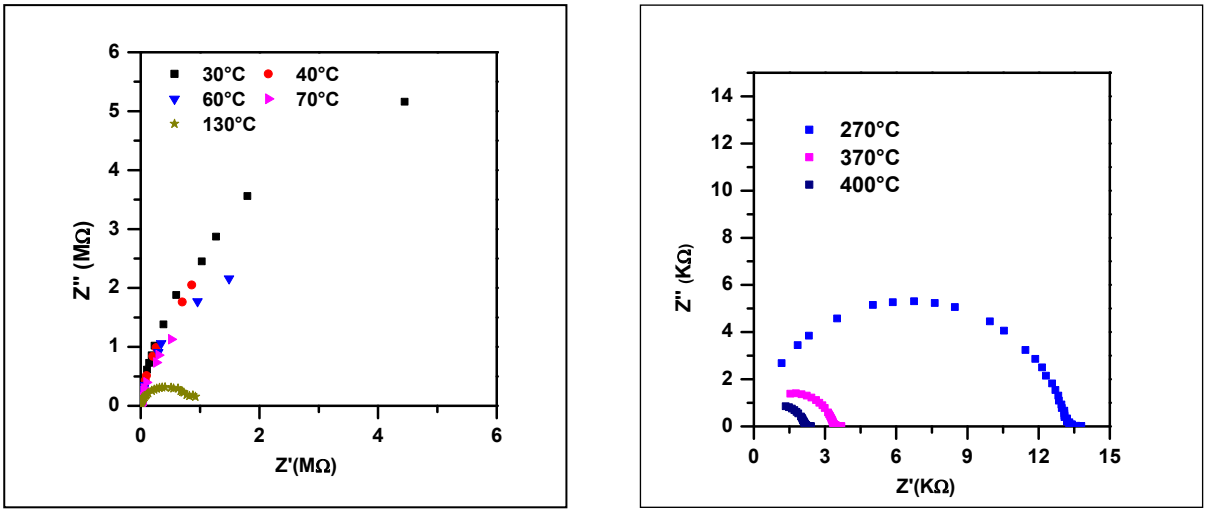
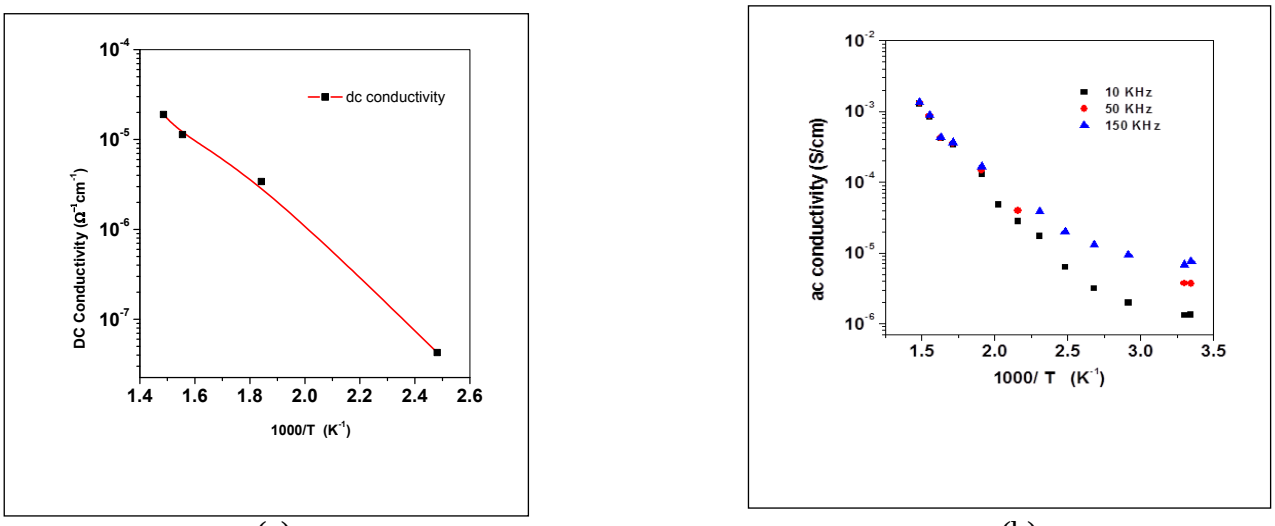


Fig. 8 Complex impedance plot of $BaMnO_3$ at different temperatures.

Fig.8 shows the Nyquist plot (i.e, variation of Z' (ω) with respect to of Z''(ω)) with different temperature. At lower temperatures, the trend of formation of semi-circular arc is observed, whereas at higher temperature the semi-circular arc is clearly visible. Throughout the temperature range of investigation, the presence of single semi-circular arc is due to the bulk properties of the material. The intercept of the semi-circular arc on the real axis give rise to bulk resistance of the material. It is observed that bulk resistance decreases with increase in temperature.

7.4.4.Temperature dependent DC and AC conductivity:



(a) (b)

Fig.9 Temperature dependent (a) DC conductivity (b) AC conductivity

Fig. 9(a) shows the variation of DC Conductivity with inverse of absolute temperature. The graph shows that conductivity decreases with increase in temperature. The temperature dependent DC conductivity can be explained using phenomenological Arrhenius equation the $\sigma_{dc} = \sigma_0 \exp(-E_a/kT)$, where Ea is the activation energy, k is the Boltzmann constant. The activation energy can be calculated form the slope of the graph.

Fig. 9(b) shows the variation of AC Conductivity of$BaMnO_3$ as a function of temperature at different frequencies. AC conductivity decreases with increase in temperature and can also be explained by above Arrhenius equation. The activation energy can also be calculated from the slope of the graph. Both the temperature dependent of AC and DC conductivities are attributed to the thermally activated process of conductivity in the materials.

CONCLUSION: CHAPTER 8

In the present study, $BaMnO_3$ perovskite ceramic oxide has been prepared using high temperature solid state reaction route. The structural (XRD), microstructural (FESEM), compositional(EDX) and dielectric properties of the proposed compounds have been studied extensively.

Based on the results obtained, following conclusions have been made:

1. X-ray diffraction technique confirms the formation of compound.
2. Field Emission Scanning Electron Micrograph (FESEM) shows that (i) Non-homogenous distribution of grains ranging from 1-1.5μm (ii) The compound is well sintered and densely packed.
3. Energy Dispersive X-ray (EDX) analysis shows that all the elemental constituents are present.
4. The temperature dependent dielectric properties showed the evidence of relaxor behaviour. The loss tangent is found to be increased with increase in temperature. DC and AC conductivity decreases with increase in temperature, which is typical behaviour of semiconductor.

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